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FINAL REPORT

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DSS CONTRACT # 23440-9-9129/01-SQ

Entitled: Study on the Use of the Hydrogenese Test to Detect H_2S Production in Oil Storage and Processing Facilities.

Respectfully submitted

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MICROMEDIA

EXECUTIVE SUMMARY

Many oilfields that initially have low H_2S levels in their oil, gas, and water phases, gradually develop higher levels of this dangerous and corrosive gas. After they initiate secondary recovery operations and as their production facilities become contaminated with H_2S - producing microorganisms, so-called "sour" production can result. This problem has already necessitated the extensive ($2 million) replacement of downhole tubing and surface facilities with H_2S - resistant alloys in Esso's Judy Creek operations.

The detection of H_2S - producing bacteria is conventionally accomplished by complicated anaerobic culturing of planktonic bacteria; these methods require 2-3 weeks to confirm presence or absence of the bacteria. These tests are cumbersome, especially when biocide treatments have been used to kill the H_2S - producing bacteria and the operators do not know whether they have been successful for 2-3 weeks. We have invented a sampling device (Robbins Device) that facilitates the collection of the pipe wall associated bacteria population. We have also developed an enzyme based (Hydrogenase) test that detects H_2 consuming (corrosive) bacteria in two to four hours. The device and the test were originally designed for the detection and control of microbial corrosion, but we reasoned that they would also be effective in the detection and control of H_2S - producing organisms. In the current study, we have shown that the device is ideally suited to sample H_2S - producing populations and the test is very accurate and very sensitive in the detection of H_2S - producing bacteria. Furthermore, this convenient and rapid field test yields negative data when these souring populations have been controlled by cleaning and/or biocide application.

The Robbins Device and the Hydrogenase Test are manufactured by Caproco (1987) Ltd. (Edmonton) under license from Microbios Ltd. and University Technologies Ltd. (Calgary), and we undertake to encourage the use of this technology throughout the Canadian petroleum community. We will, with the permission of the Crown, disseminate these present data via our new NSERC Industrial Research Chair in Biofilm Microbiology and via the University Panel of the Alberta Oilsands Technology and Research Authority (AOSTRA).

SOMMAIRE EXECUTIF

Plusieurs gisements de pétrole ou de gaz avec de faibles concentrations initiales de H_2S produisent des concentrations graduellement plus élevées de ce gaz corrosif et dangereux. Ce problème est dû à l'activité de microorganismes tels que les bactéries sulfatoréductrices. Ce problème a requis le remplacement de matériaux tubulaires et autres équipements avec des alliages d'aciers (pour une valeur de deux millions de dollars) dans les opérations de Esso à Judy Creek en Alberta.

Les bactéries sulfatoréductrices sont détectées conventionnellement à l'aide de méthodes de mise en culture lentes et compliquées. Il faut souvent attendre deux ou trois semaines avant de pouvoir confirmer la présence des bactéries. Ces méthodes sont particulièrement encombrantes lorsque des biocides furent ajoutés pour combattre les bactéries qui produisent le H_2S.

Nous avons inventé un mécanisme (Robbins Device) pour faciliter l'échantillonnage du biofilm qui voile la surface des conduits. Nous avons aussi développé une méthode rapide (Hydrogenase Test) d'analyse des enzymes produites par les communautés bactériennes corrosives qui consomment l'hydrogène. Bien que ces systèmes furent développés pour la détection et le contrôle de la corrosion bactérienne, nous avions lieu de croire qu'ils pourraient aussi être appliqués à la détection et le contrôle des bactéries qui produisent l'hydrogène sulfuré. Dans la présente étude nous avons montré que l'appareil Robbins convient à l'échantillonnage des communautés produisant le H_2S et que le test de l'hydrogénase est rapide et fiable dans la détection de ces populations bactériennes. De plus, ce test commode produit rapidement des résultats négatifs quand les populations qui produisent l'hydrogène sulfuré ont été détruites par l'action des nettoyages mécaniques ou chimiques.

Le Robbins Device et le Hydrogenase Test sont fabriqués par Caproco (1987) Ltd. d'Edmonton sous license de Microbios Ltd. et University Technologies Ltd. de Calgary. Nous nous chargeons d'encourager l'adoption de cette technologie par la communauté du pétrole au Canada. Avec la permission de la Couronne, nous désirons faire circuler les données de cette étude par voie de notre chaire (NSERC Industrial Research Chair in Biofilm Microbiology) et grâce au University Panel of the Alberta Oil Sands technology and Research Authority.

BACKGROUND

When an oilfield is sweet (low H_2S), when it is first exploited, all of the downhole well tubing and the surface facilities are made of mild steel for reasons of economy. Most sweet systems remain low in H_2S during primary recovery, when oil is driven to the surface by natural gas pressure, but the injection of water that constitutes the beginning of secondary recovery often starts a process wherein H_2S-producing bacteria are introduced into both the reservoir and the production system and they become sour (high H_2S). Bacteria can generate levels of H_2S that exceed 16,000 ppm, in heavily contaminated sytems, and mild steel must be replaced with much more expensive H_2S-resistant alloys when levels consistently exceed ± 200 ppm. When samples indicate that H_2S levels exceed these metalurgical minima an extensive sampling program must be undertaken to locate the offending organisms (reservoir and/or specific production facilities) and to determine whether the biological problem can be solved by killing the bacteria with biocides or whether all of the steel in the operation must simply be replaced. Esso Resources Canada Ltd. has recently replaced much of its facilities at Judy Creek, at a cost of > 2 million dollars, and dozens of other aging secondary operations in Alberta are facing the same decision.

At present testing for H_2S-producing bacteria, which are called Sulphate-Reducing Bacteria (SRB), involves growing these strictly anaerobic organisms in special media and these tests yield results in 2-3 weeks because of the slow growth rate of these bacteria. Biocide treatments are especially ill-served by this test method because serial treatments can only be based on data that takes 2-3 weeks to generate. Recently, with support from the CRD program of the Targetted Research Section of NSERC, we developed a rapid enzyme-based test for the detection of corrosion-causing bacteria, some of which are SRB. This very rapid (2-4 hour) test is based on the detection of the hydrogenase enzyme that is found in all H_2S-producing SRB, and the test yields negative data when the bacteria have been killed and their hydrogenases have been denatured. We therefore resolved, in this contract, to assess this rapid and very simple hydrogenase test for its suitability in detecting H_2S-producing bacteria and for the assessment of the efficacy of biocides used to control these souring organisms.

OBJECTIVES

1. Test the efficacy of the hydrogenase test kit in detecting SRB in scrapings taken from surfaces in souring process facilities.
2. Install Robbins Device studs in problem areas and determine their optimum locations and optimal contact times for SRB biofilm detection.
3. Obtain longitudinal data on Robbins Device studs and the hydrogenase test to assess this combination in SRB detection and in the assessment of clean-up and biocide remediation.

PROGRESS TOWARDS SPECIFIC OBJECTIVES

All of the stated objectIves of this study have been achieved.

Objective 1 - In the initial part of this study we obtained 103 surface scraping samples from a souring oil production facility near Calgary and we processed these samples by both the traditional culture method (Butlin's Medium) and the new hydrogenase test kit (Table 1).

Table 1 - Comparison of Culture Methods (Butlin's Medium) with the New Hydrogenase Test in the Detection of H_2S-producing Bacteria.

Hydrogenase	Culture Method	# of Samples
Positive	Positive	62
Positive	Negative	7
Negative	Positive	0
Negative	Negative	34

The hydrogenase method proved to be very accurate in that it was positive in 62 cases where the cultures were positive and negative in 34 cases where the cultures were negative. The hydrogenase test proved to be very sensitive in that it yielded positive results in 7 cases where the cultures were either negative or too weakly positive to be scored as positive. The hydrogenase test was never negative when cultures yielded positive results. We conclude that this new very rapid enzyme-based test is more accurate and more sensitive than culture methods in the detection of the SRB that cause H_2S production in oil recovery operations.

Objective 2 - Because bacterial H_2S formation involves the formation of complex metabolically-integrated consortia of SRB and other organisms, most souring communities are associated with the highly organized microbial population on surfaces. For this reason we have concentrated on surface (sessile) samples obtained initially by scraping available metal surfaces (valve housings, corrosion coupons), and later on the surfaces of Robbins Device studs installed in souring systems. An analysis of the location of the 69 samples yielding strongly positive results (Objective 1) showed that they tended to be from low flow areas (eg. dead legs), and from areas with high water contents that favor bacterial growth. These "worst case" areas were chosen for the installation of Robbins Devices in 4 souring oil producing facilities near Calgary.

In all 4 systems one set of Robbins Devices were installed in the bottom of the Free Water Knock Out (FWKO) that receives oil and produces water from the field itself. Further Robbins Devices were installed in Oil Treater Vessels (Treaters). In two systems (A and B) we were able to install one set of these sessile sampling

devices near the input pipe and in the oil phase in addition to another set at the worst case location near the drain plug. In the other two surface facilities C and D we were only able to install sampling devices in the worst case location near the drain plug. Individual sample studs were withdrawn from all of these multistud devices, for hydrogenase testing, at weekly intervals in order to determine the length of time that the sessile sampling device has to be in place before it was fully colonized. The data are represented in Table 2.

Table 2

Hydrogenase Test data on sessile samples form 4 surface facilities.

System	1 week	2 weeks	3 weeks	4 weeks	8 weeks
A FWKO	-	-	-	-	-
Treater - oil phase	-	-	-	-	-
- bottom	++	++	++++	++++	++++
B FWKO	-	-	-	-	-
Treater - oil phase	-	-	-	-	-
- bottom	-	+	-	++	++
C FWKO	-	-	+	++	++
Treater - bottom	+	++	++++	++++	++++
D FWKO	-	-	-	-	-
Treater - bottom	-	-	-	-	-

These data show that sample location is of paramount importance in the detection of sessile H_2S - producing bacterial populations, in that ++ levels of activity in the bottom of a treater could be associated (System A) with negative data from the oil phase of the same treater and from the Free Water Knock Out (FWKO) of the same system. Generally, strongly souring systems (Systems A and C) developed representative sessile populations of SRB on the studs of Robins Devices within 2 weeks but 4 weeks were required to stabilize the colonization of sample studs in less actively souring systems (System B).

Objective 3 - In order to assess the usefulness of the hydrogenase test in the assessment of the efficacy of biocides and cleaning in the control of H_2S production problems, we treated the 4 souring systems (A-D) in the following ways (Table 3).

Table 3

Longitudinal Data in the Efficacy of Various Biofilm Control Measures as Measured by the Hydrogenase Test.

System Location	Treatment	Time 0[3]	1 day	2 days	4 days	1 week	2 weeks	3 weeks	4 weeks
A FWKO	Cleaning	-	-	-	-	-	-	-	-
Treater-oil	and biocide	-	-	-	-	-	-	-	-
-bottom	slug dose[1]	++++	-	-	-	-	++	++++	++++
B FWKO	Continuous[2]	-	-	-	-	-	-	-	-
Treater -oil	biocide	-	-	-	-	-	-	-	-
-bottom	application	++	++	++	++	+	-	-	-
C FWKO	Biocide	++	+/-	-	-	+/-	+	++	++
Treater-bottom	Slug dose[1]	++++	+	-	-	+	+++	++++	++++
D FWKO	Untreated	-	-	-	-	-	-	-	-
Treater -bottom	Control	-	-	-	-	-	-	+	++

1. Slug dose = 200 ppm of a proprietary liquid biocide
2. Continuous Dose = 15 ppm of a proprietary liquid biocide
3. Before treatment (5-30 minutes)

The treater bottom sample in System D, which was untreated, developed a 1+ reaction at week 3 (week 11 if the studies in Tables 2 and 3 are combined) and a 2+ reaction at week 4 (week 12). When a colonized system (System B) was treated continuously with a low dose (15 ppm) of Biocide the sessile SRB persisted as live cells for 1 week but were well controlled thereafter. Cleaning followed by slug dose biocide treatment (Sytem A) caused a more rapid (< 1 day) disappearance of hydrogenase activity than a slug dose alone (System C), and sessile SRB activity was reestablished more rapidly in the system (C) that was not cleaned. It is clear from these data that the hydrogenase test is sufficiently acurate and sensitive to detect the presence of SRB in sessile samples and to detect the demise of these H_2S-producing organisms when they are killed by biocides.

CONCLUSIONS

1. The very rapid hydrogenase (2-4 hour) test was found to be more accurate and more sensitive than the much slower (2-3 week) culture method for the detection of H_2S-producing SRB.

2. Robbins Devices were found to be ideally suited for the detection of sessile SRB by the hydrogenase test, and they were most effective if located in low flow water rich "worst case" areas and allowed to colonize for 2-4 weeks.

3. Longitudinal data from Robbins Devices installed in worst case areas of 4 souring systems showed that the control of H_2S-production activity by biocide killing of SRB can be readily and rapidly detected by a combination of the Robbins Device and Hydrogenase Test technologies.

COMMERCIAL APPLICATIONS

The Robbins Device is manufactured by Caproco Ltd. (Edmonton) under license from Microbios Ltd., and the Hydrogenase Test Kit® is manufactured by the same company under a sublicense from B.P. Resources Canada Ltd. which licences the technology from University Technologies Inc. of the University of Calgary. Both products are well established in the corrosion detection and control area and both are selling at a very satisfactory rate.

This present demonstration that the Robbins Device and the Hydrogenase Test are very useful in the detection and control of microbial souring of production facilities has stimulated great interest in our sponsoring companies (Esso Resources and B.P. Canada). We also have preliminary enquiries from Sea-Land Testing Ltd. concerning the systematic use of the Hydrogenase Test in screening backflow water from water injection wells in all sweet fields to detect bacterial souring before it becomes a serious economic problem. This technology will be diseminated amongst the four oil companies that support our NSERC Industrial Research Chair in Biofilm Microbiology and amongst the eight oil companies that are members of the University Panel of the Alberta Oilsands Technology and Research Authority (AOSTRA).